Langevin dynamics of a polymer with internal distance constraints

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We present a rigorous approach to the Langevin dynamics of ideal polymer chains subject to internal distance constraints. The permanent constraints are modeled by harmonic potentials in the limit when the strength of the potential approaches infinity (hard cross-links). The cross-links are assumed to exist between arbitrary pairs of monomers. Formally exact expressions for the resolvent and spectral density matrix of the system are derived. To illustrate the method we study the diffusional behavior of monomers in the vicinity of a single cross-link within the framework of the Rouse model. The same problem has been studied previously by Warner [J. Phys. C **14**, 4985 (1981)] on the basis of Lagrangian multipliers. Here we derive the full, hence exact, solution to the problem. [S1063-651X(97)09702-X]

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I. INTRODUCTION

A theoretical treatment of the dynamics of polymer networks is a generally unsolved problem. In a preliminary attempt Edwards *et al.* [1,2] studied the problem of a polymer subject to internal distance constraints. In their investigation the underlying theoretical problem was to handle the quenched degrees of freedom (hard cross-link constraints) which, for example, in a random network exist between pairs of arbitrary polymer segments (the monomers). As a first step Edwards considered a (macroscopically) long polymer chain which was internally cross-linked to itself at random. The polymer backbone was assumed to be Gaussian and the resulting dynamics was found to be of the standard Rouseian type [3,4]. Permanent junction points were treated by Lagrangian multipliers, which led to enormous technical difficulties for the corresponding differential equations. In fact, these could only be handled by strong approximations, such as preaveraging in combination with harmonic variations. Even when the problem was highly oversimplified and only one cross-link was considered the method of Lagrangian multipliers still becomes highly involved, as was pointed out in a successive paper by Warner [5].

The purpose of the present paper is to develop an alternative formalism for treating Langevin dynamics of polymers subject to internal distance constraints. For calculational simplicity the simplest working model for a free polymer, the Rouse model [3,4], is considered. It is suggested that the more complicated problem of a random network can also be treated *exactly* by the presented method. We adopt here the minimal model suggested by Edwards [1,2] and consider one (macroscopically) huge polymer chain which is randomly cross-linked to itself. Such a cross-linking process will lead to tetrafunctional cross-links. In previous works we have already demonstrated that the analogous static problem can be solved exactly when excluded volume effects between the polymer segments are ignored [6,7]. Physical quantities such as the static structure factor or the radius of gyration were found to be self-averaging and could be determined by relatively simple numerical means. The essential trick was to account for the cross-links in a general connectivity matrix that includes both the connectedness of the polymer chain *and* an additional contribution from the cross-linking. In close analogy we expect the corresponding dynamic problem to have a similar exact solution as long as complicating factors such as excluded volume, hydrodynamic forces, or entanglements are neglected. To demonstrate this analogy we start from the standard Langevin description for the polymer segments and solve the stochastic differential equation in terms of its resolvent. As an instructive example we reconsider the figure-eight-shaped polymer problem (i.e., a polymer ring with one cross-link) studied by Warner [5] and present its full solution. We first confirm the results from Warner, which have been derived only for low frequencies and low Rouse mode index, but show secondly the exact solution in the entire frequency and mode domain. Moreover, the technique introduced here opens new ways to study Langevin dynamics of constrained systems.

The paper is organized as follows. In Sec. II the physical model, a generalized version of the Rouse model with internal distance constraints, is introduced. Section III summarizes some of the basic theorems regarding Langevin dynamics to be used later on. In Sec. IV, the main calculational body of the paper, the general mathematical formalism for handling internal distance constraints is developed in detail. Our treatment is a generalization of a method previously developed for computing statistical properties of randomly cross-linked Gaussian structures, i.e., ideal polymer networks [6,7]. In Sec. V an application of the method to diffusional motion of a single cross-link is given (the Warner problem). Section VI contains a short discussion of main results and outlook.

II. ROUSE MODEL WITH INTERNAL DISTANCE CONSTRAINTS

As a minimal model for the dynamics of a Gaussian chain subject to internal distance constraints we consider a generalized version of the classical Rouse model [3]. Its discrete version is a bead-spring model, where the motion of the

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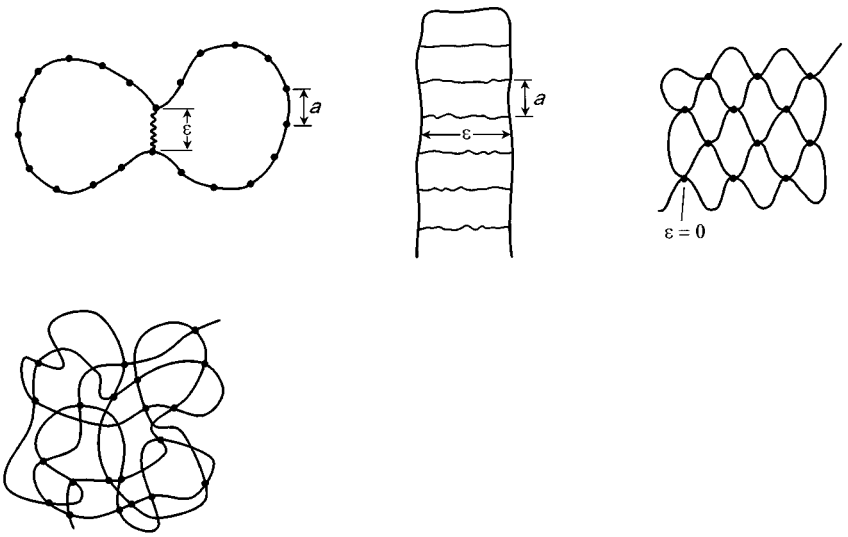

FIG. 1. Examples of different cross-linking topologies. (a) The polymer shape discussed in Sec. V. a is the persistence length of the polymer backbone. The hard cross-link constraint is enforced by $\varepsilon \to 0$. (b) A ladder-shaped polymer with $\varepsilon \neq 0$. (c) Two-dimensional membrane. (d) Random network.

beads (monomers) is governed by the coupled set of Langevin equations

$$\zeta \frac{d\mathbf{R}_i(t)}{dt} = -\nabla_{\mathbf{R}_i} \mathcal{H}_0(\{\mathbf{R}_i\}) + \mathbf{F}_i(t). \tag{1}$$

In this equation of motion the inertial term is omitted as usual. ζ denotes the inverse mobility or friction constant, and $\mathbf{R}_i(t)$ $(i=0,\ldots,N)$ are the trajectories of the monomers in three-dimensional space. The stochastic forces $\mathbf{F}_i(t)$ are assumed to be δ correlated with first and second moments given by [4]

$$\langle F_i^\alpha(t) \rangle = 0, \tag{2}$$

$$\langle F_i^\alpha(t) F_j^\beta(t') \rangle = 2\zeta k_B T \delta_{ij} \delta_{\alpha\beta} \delta(t-t').$$

Superscripts $\alpha,\beta = x,y,z$ represent the three-dimensional Cartesian coordinates. In the classical Rouse model excluded volume interaction and hydrodynamic forces are disregarded and only elastic forces between monomers are retained in the Hamiltonian. Here we consider a more general form of the Rouse model with an extra potential to allow for modeling the internal distance constraints

$$\beta \mathcal{H}_0 = \frac{3}{2a^2} \sum_{i=1}^{N} (\mathbf{R}_i - \mathbf{R}_{i-1})^2 + \frac{3}{2\varepsilon^2} \sum_{e=1}^{M} (\mathbf{R}_{i_e} - \mathbf{R}_{j_e})^2. \tag{3}$$

The first term in the Hamiltonian represents the connectivity of a Gaussian chain with persistence length a, whereas the second term models the cross-links. In particular we are concerned with permanent constraints when a monomer, say i_1, is linked to another monomer labeled by j_1. For more than one cross-link a whole set C of cross-link ''coordinates'' is needed to specify all junctions in the system

$$C = (i_1, j_1), \ldots, (i_e, j_e), \ldots, (i_M, j_M). \tag{4}$$

For example, depending on C the object under investigation can be a flexible ring polymer, a two-dimensional membrane, or a rubber network (Fig. 1).

Although the theory will be developed for arbitrary coupling constant ε two scenarios are of special relevance. For $\varepsilon \to 0$ it has been shown [6] that the Hamiltonian (3) is suitable to model hard δ constraints (the classical cross-links) of the form

$$\prod_{e=1}^{M} \delta(\mathbf{R}_{i_e}(t) - \mathbf{R}_{j_e}(t)). \tag{5}$$

The case $\varepsilon \to \infty$ leads to the well-known problem of a free chain, which serves here as a reference state. One might be worried that the above model is ill defined and might diverge in the limit $\varepsilon \to 0$. It will be shown in Sec. IV that the converse is true and that a surprisingly simple solution can be obtained for this special limit. As shown in the earlier paper on the static properties [6], it is important to take the limit $\varepsilon \to 0$ at the very end of the calculation. This procedure ensures firstly that no mathematical problems occur and secondly that in this case hard cross-link constraints is treated properly. Before going into more of the calculational details some of the basic definitions and notations regarding Langevin dynamics are summarized in the next section.

III. LANGEVIN DYNAMICS OF IDEAL POLYMERS: PRELIMINARIES

Consider the generalized Ornstein-Uhlenbeck process specified by Eqs. (1)–(3). For calculational simplicity matrix notation will be used. We define $(N+1)$-dimensional ''supervectors'' with three-dimensional vector components to account for the positions of all monomers $\mathbf{R}(t) = (\mathbf{R}_0(t), \ldots, \mathbf{R}_N(t))^\dagger$ and for the stochastic forces acting upon them $\mathbf{F}(t) = (\mathbf{F}_0(t), \ldots, \mathbf{F}_N(t))^\dagger$. The dagger denotes the complex conjugate of the transposed vector. Furthermore, the $(N+1)$-dimensional connectivity (Kirchhoff) matrix is introduced as

$$\mathcal{M}(z) = \omega_0 \left(\mathcal{W}_0 + \frac{1}{z} \sum_{e=1}^{M} \mathcal{X}(i_e, j_e) \right), \tag{6}$$

where

$$\mathcal{W}_0=\begin{pmatrix} 1 & -1 & 0 & \cdots & 0 \\ -1 & 2 & -1 & & \vdots \\ 0 & \ddots & \ddots & \ddots & 0 \\ \vdots & & -1 & 2 & -1 \\ 0 & \cdots & 0 & -1 & 1 \end{pmatrix} \tag{7}$$

is the Wiener matrix associated with the polymer ''backbone,'' and

$$\mathcal{X}(i_e,j_e)$$
$$=\begin{pmatrix} 0 & 0 & \cdots & 0 & \cdots & 0 & 0 \\ \vdots & \vdots & & 0 & & \vdots & \vdots \\ 0 & 1 & & \vdots & & -1 & 0 \\ 0 & 0 & \cdots & 0 & \cdots & 0 & 0 \\ 0 & -1 & & \vdots & & 1 & 0 \\ \vdots & \vdots & & 0 & & \vdots & \vdots \\ 0 & 0 & \cdots & 0 & \cdots & 0 & 0 \end{pmatrix} \begin{matrix} \vdots \\ \leftarrow i_e\text{th row} \\ \vdots \\ \leftarrow j_e\text{th row} \\ \vdots \end{matrix} \tag{8}$$

models a single cross-link. For further use we note that a characteristic time scale is given by the inverse of the ''frequency''

$$\omega_0=\frac{3k_BT}{a^2\zeta}. \tag{9}$$

The dimensionless parameter $z=(\varepsilon/a)^2$ in Eq. (6) is used to enforce the cross-linking constraints. With the above definitions the system of stochastic differential equations (1) cast into matrix form reads

$$\frac{d\mathbf{R}(t)}{dt}+\mathcal{M}(z)\mathbf{R}(t)=\frac{1}{\zeta}\mathbf{F}(t). \tag{10}$$

Some of the physical quantities of interest and their interrelations are listed below. More details can be found, for example, in Ref. [8]. The Green's function to Eq. (10) is given by

$$\mathcal{G}(t)=\lim_{z\to 0} e^{-\mathcal{M}(z)t}. \tag{11}$$

For $z\to 0$ the case of hard δ constraints is recovered. Otherwise z is an additional distance parameter in the model. Of great importance in the following derivation is the Laplace transform (resolvent) of the matrix $\mathcal{M}$

$$\mathcal{R}(\omega)\equiv\int_0^\infty dt\, e^{-i\omega t}\mathcal{G}(t)=\lim_{z\to 0}[i\omega\mathcal{I}+\mathcal{M}(z)]^{-1}, \tag{12}$$

where $\mathcal{I}$ denotes the identity matrix.

From Eq. (2) the spectral matrix of the Langevin forces $\mathbf{F}(t)$ is found to be

$$\langle\tilde{\mathbf{F}}(\omega)\tilde{\mathbf{F}}^\dagger(\omega')\rangle=12\pi k_BT\zeta\delta(\omega-\omega')\mathcal{I}, \tag{13}$$

where

$$\tilde{\mathbf{F}}(\omega)=\int_{-\infty}^{\infty} dt\, e^{-i\omega t}\mathbf{F}(t) \tag{14}$$

is the Fourier transform of the stochastic forces. By $\mathbf{F}_i\mathbf{F}_j$ we mean the usual three-dimensional scalar vector product, whereas $\mathbf{F}\mathbf{F}^\dagger$ is used for outer vector products. Fourier transforms are denoted by a tilde.

A formal solution to Eq. (10) can be obtained by Rice's method [8]. The spectral density matrix for the stochastic variable $\mathbf{R}(t)$ can be derived by use of Eq. (13) and Fourier transformation of Eq. (10),

$$\langle\tilde{\mathbf{R}}(\omega)\tilde{\mathbf{R}}^\dagger(\omega')\rangle=12\pi D\,\delta(\omega-\omega')\mathcal{R}(\omega)\mathcal{R}^\dagger(\omega'), \tag{15}$$

with the diffusion coefficient D given by

$$D=k_BT/\zeta. \tag{16}$$

Of primary interest for the diffusional behavior is the two-time correlation function matrix defined as

$$\mathcal{C}(t,t')=\langle[\mathbf{R}(t)-\mathbf{R}(t')][\mathbf{R}(t)-\mathbf{R}(t')]^\dagger\rangle. \tag{17}$$

Finally, a steady-state solution for $\mathcal{C}(t,t')$ in terms of the resolvent (12) is easily derived from the expression for the spectral density matrix in Eq. (15),

$$\mathcal{C}(t-t')=\frac{12D}{\pi}\int_0^\infty d\omega[1-\cos\omega(t-t')]\mathcal{R}(\omega)\mathcal{R}(\omega)^\dagger. \tag{18}$$

In the following study our primary goal will be to find a general approach to calculate the resolvent $\mathcal{R}(\omega)$, Eq. (12), for an arbitrary set of cross-linking constraints C, Eq. (4). From there Green's function and correlation functions can in principle be obtained by use of the standard formulas presented in this section. Although $\mathcal{M}(z)$ is a matrix which highly depends on all the details of C (the cross-link positions), substantial progress can be made by invoking the following exact method.

IV. CALCULATION OF THE RESOLVENT $\mathcal{R}(\omega)$

The first step in deriving a general expression for $\mathcal{R}(\omega)$ for hard cross-links is to find a way to perform the limit $z\to 0$ in Eq. (12). This is an interesting problem in its own right which so far could only been handled by introducing a finite cutoff at $z=1$ and successive crude variational estimates. Here we present an analytically exact approach that can overcome these difficulties. The mathematical trick is to utilize an additional symmetry of the cross-link term in Eq. (8) by writing the complete cross-link contribution in Eq. (6) in the form of a dyadic (outer vector) product

$$\sum_{e=1}^{M}\mathcal{X}(i_e,j_e)=\mathcal{U}\mathcal{U}^\dagger, \tag{19}$$

where

$$\mathcal{U}(C)\equiv(\mathbf{u}_1,\ldots,\mathbf{u}_M) \tag{20}$$

has been introduced as the $(N+1)\times M$ rectangular matrix with each of its M column vectors given by

$$\mathbf{u}_e = \mathbf{e}_{i_e} - \mathbf{e}_{j_e} \quad (e = 1, \ldots, M). \tag{21}$$

Here $\mathbf{e}_{i_e}$ represents the $(N+1)$-dimensional unit vector with 1 in the i_eth position, and 0 otherwise. Thus $\mathcal{U}(C)$ has only $2M$ elements not equal to zero that contain complete information about all cross-link positions. In the above notation each cross-link is uniquely represented by a vector $\mathbf{u}_e$. Note that all vectors $\mathbf{u}_e$, $e = 1, \ldots, M$ are linearly independent for tetrafunctional cross-links. Combining Eqs. (6), (12), and (19), the resolvent cast in matrix form reads

$$\mathcal{R}(\omega) = \frac{1}{\omega_0} \lim_{z \to 0} \left(i \frac{\omega}{\omega_0} \mathcal{I} + \mathcal{W}_0 + \frac{1}{z} \mathcal{U} \mathcal{U}^\dagger \right)^{-1}. \tag{22}$$

It is convenient to decompose Eq. (22) into a singular and a nonsingular part, with the nonsingular part being

$$\mathcal{W} = i \frac{\omega}{\omega_0} \mathcal{I} + \mathcal{W}_0. \tag{23}$$

It is well known in the mathematical literature that if the inverse of $\mathcal{W}$ exists, then the inverse in Eq. (22) is given by

$$\left(\mathcal{W} + \frac{1}{z} \mathcal{U} \mathcal{U}^\dagger \right)^{-1} = \mathcal{W}^{-1} [\mathcal{I} - \mathcal{U} (z\mathcal{I} + \mathcal{U}^\dagger \mathcal{W}^{-1} \mathcal{U})^{-1} \mathcal{U}^\dagger \mathcal{W}^{-1}]. \tag{24}$$

This theorem can be directly verified by matrix multiplication. The latter identity is also known as the Sherman-Morrison formula [9].

A. The limit $z \to 0$

There are two subtle points about the existence of the right hand side of Eq. (24). First, we require $\mathcal{W}^{-1}$ to exist. The only critical case arises if $\omega = 0$, i.e., when $\mathcal{W} = \mathcal{W}_0$ in Eq. (23). The problem here is that $\mathcal{W}_0$ is only positive *semidefinite* and there is one mode with eigenvalue 0 from translational invariance. This can be directly seen from the definition of $\mathcal{W}_0$ in Eq. (7), which is a row (column) constant matrix. However, even in the semidefinite case the above theorem remains valid if $\mathcal{W}^{-1}$ denotes a generalized inverse of $\mathcal{W}$ as was proved in Ref. [10].

Secondly, from the definition of $\mathbf{u}_e$ in Eq. (21) it is easily verified that for tetrafunctional cross-links all M vectors $\mathbf{u}_e$ are linearly independent. Thus in general the kernel $z\mathcal{I} + \mathcal{U}^\dagger \mathcal{W}^{-1} \mathcal{U}$ will be a *positive* definite matrix of dimension M and *full* rank which has only positive eigenvalues for all non-negative values of z. As a consequence performing the $z \to 0$ limit in Eq. (24) leads to a well-defined expression for the resolvent

$$\mathcal{R}(\omega) = \frac{1}{\omega_0} \mathcal{W}^{-1} [\mathcal{I} - \mathcal{U} (\mathcal{U}^\dagger \mathcal{W}^{-1} \mathcal{U})^{-1} \mathcal{U}^\dagger \mathcal{W}^{-1}]. \tag{25}$$

The first term is the linear chain (Rouse) model, whereas the second part arises entirely from the effect of cross-linking. Although the case of general cross-linking potential z is still implicit in the basic formula (24), we will restrict ourselves in the following discussion to the somewhat simpler case $z = 0$, i.e., hard δ constraints. Equations (24) and (25) are formally exact solutions to the problem posed in Eqs. (1)–(4). The further evaluation of $\mathcal{R}(\omega)$ for specific realizations of cross-links C can be split into two parts and is discussed in subsequent sections.

B. Resolvent of $\mathcal{W}_0$

Evaluation of the inverse of $\mathcal{W}$ in Eq. (25) can in principle be done by full diagonalization of $\mathcal{W}_0$, which is tridiagonal. For calculational simplicity we consider here only the cyclic counterpart of $\mathcal{W}_0$ with periodic boundary conditions

$$\mathcal{W}_0 = \begin{pmatrix} 2 & -1 & 0 & \cdots & -1 \\ -1 & 2 & -1 & \cdots & 0 \\ \vdots & \ddots & \ddots & \ddots & \vdots \\ 0 & \cdots & -1 & 2 & -1 \\ -1 & \cdots & 0 & -1 & 2 \end{pmatrix}. \tag{26}$$

Both models (7) and (26) are known to obey the same Rouse dynamics in the limit $N \to \infty$ [11]. Physically the latter situation represents a flexible ring polymer. The eigensystem to Eq. (26) is of particular simple form since it is a circulant. The eigenvalues read

$$\lambda_k = 4 \sin^2 \frac{\pi k}{N+1}, \quad k = 0, \ldots, N. \tag{27}$$

The modal matrix of Eq. (26) is the Fourier matrix $\mathcal{F}$ [14] with matrix elements

$$[\mathcal{F}]_{kl} = \frac{1}{\sqrt{N+1}} \exp \frac{2\pi i k l}{N+1}, \quad k, l = 0, \ldots, N. \tag{28}$$

Spectral decomposition leads to the well-known representation of the inverse $\mathcal{W}^{-1}$ in terms of its eigenvalues

$$[\mathcal{W}^{-1}]_{kl} = \frac{1}{N+1} \sum_{n=0}^{N} \frac{\exp\left(\frac{2\pi i n (k-l)}{N+1} \right)}{i\omega/\omega_0 + \lambda_n}. \tag{29}$$

C. Discussion of kernel

The remaining calculational task for determining $\mathcal{R}(\omega)$ is the evaluation of the kernel function in the second part of Eq. (25),

$$\mathcal{K}(\omega; C) \equiv (\mathcal{U}^\dagger \mathcal{W}^{-1} \mathcal{U})^{-1}. \tag{30}$$

Since $\mathcal{K}(\omega; C)$ depends on all the cross-link positions $C = (i_1, j_1), \ldots, (i_M, j_M)$ via $\mathcal{U}$ no further analytical progress is possible without specifying the cross-link in the system. On the other hand, from the mathematical structure of $\mathcal{K}(\omega; C)$ most problems of interest fall into one of the following three categories. Only one of these will be considered in detail in Sec. V.

(i) The number of cross-links M is small. Since $\mathcal{K}(\omega; C)$ requires inversion of an $M \times M$ matrix, analytical progress is always possible if M is not too large. A particu-

larly simple problem is treated in the next section when we consider the dynamics of a polymer shaped like the figure of eight [Fig. 1(a)].

(ii) Another special case arises when M is large, but there is some additional pattern in the structure of $\mathcal{U}$. Examples of this kind are illustrated in Figs. 1(b) and 1(c). In particular, the sketch in Fig. 1(b) shows an example of a macromolecule with distance constraints $z\neq 0$, i.e., the more general case governed by Eq. (24). For the above examples $\mathcal{K}$ can be calculated as a consequence of the regularity of the cross-link positions. We will report on these systems in a separate publication.

(iii) The third important category arises when M is large and the cross-link positions C in Eq. (4) are picked at random. This is the case of a polymer gel [Fig. 1(d)]. Here one has to resort to numerical computation of $\mathcal{K}(\omega;C)$ [7]. However, there is still a huge calculational advantage with Eq. (25). For a polymer network we have in general $M\ll N$. Equation (25) requires ''only'' the inverse of an $M\times M$ matrix, [7] and not of the complete $N\times N$ connectivity matrix as is commonly believed in the polymer literature [12,13].

An analytic approach to the network problem would be to perform the quenched average of the resolvent over the cross-link positions C. The latter problem is a key problem in current network research and has not been analytically solved even for the static problem.

Before calculating $\mathcal{R}(\omega)$ for a specific example, we want to establish some remarkable and general properties of the operators in Eq. (25). Consider the cross-link part in Eq. (25),

$$\mathcal{V}\equiv\mathcal{W}^{-1}\mathcal{U}(\mathcal{U}^{\dagger}\mathcal{W}^{-1}\mathcal{U})^{-1}\mathcal{U}^{\dagger}\mathcal{W}^{-1}. \tag{31}$$

By elementary matrix multiplication it is found that

$$\mathcal{V}\mathcal{W}\mathcal{V}=\mathcal{V},\quad \mathcal{U}^{\dagger}\mathcal{V}=\mathcal{U}^{\dagger}\mathcal{W}^{-1},\quad \mathcal{V}\mathcal{U}=\mathcal{W}^{-1}\mathcal{U}. \tag{32}$$

A matrix with these properties is said to be a generalized projector to $\mathcal{W}^{-1}$. Furthermore,

$$(\mathcal{W}\mathcal{V})^2=\mathcal{W}\mathcal{V},\quad (\mathcal{V}\mathcal{W})^2=\mathcal{V}\mathcal{W} \tag{33}$$

are idempotents whose eigenvalues are known exactly: $\lambda_1=1$ and $\lambda_2=0$ with degeneracies M and $N-M$. By use of the above results it is easy to prove that the resolvent satisfies a remarkable orthogonality relation

$$\mathcal{U}^{\dagger}\mathcal{R}(\omega)=\mathcal{R}(\omega)\mathcal{U}=0. \tag{34}$$

Equation (34) is valid for arbitrary cross-link positions C and independent of the specific cross-link topology of the system under investigation.

V. DIFFUSIONAL MOTION OF A SINGLE CROSS-LINK

As the simplest possible application of the method developed in Sec. IV we consider the figure-eight-shaped polymer depicted in Fig. 1(a). What we have in mind is to model the dynamics of a single cross-link in an ideal dilute network when the distance between cross-links is large [5]. It is expected that monomers in the neighborhood of the cross-link are somewhat affected by the slower dynamics of the cross-link [1,5,15].

A suitable realization of the system in Fig. 1(a) would be

$$\mathcal{U}(C)=\mathbf{u}_1=\mathbf{e}_0-\mathbf{e}_{(N+1)/2}. \tag{35}$$

That is, monomer 0 is linked to monomer $(N+1)/2$. The main calculational task is to determine the kernel function, Eq. (30), of the system. From Eq. (35) and with $\mathcal{W}^{-1}$ given by Eq. (29) we get immediately

$$\mathcal{K}(\omega)=\left(\frac{4}{N+1}\sum_{n\ odd}\frac{1}{i\omega/\omega_0+\lambda_n}\right)^{-1}, \tag{36}$$

where the summation includes only the odd terms. For the diffusional motion the quantity of interest is the self-correlation function contained in the diagonal elements of the correlation matrix (18)

$$[\mathcal{C}(t-t')]_{ss}=\langle[\mathbf{R}_s(t)-\mathbf{R}_s(t')]^2\rangle, \tag{37}$$

where s is the distance of the sth monomer with respect to the cross-link at position $s=0$. Typical terms and manipulations in the straightforward derivation which is not carried out in detail are of the form

$$\begin{aligned}\frac{1}{N+1}\sum_{n\,odd}\frac{\exp\left(\frac{2\pi isn}{N+1}\right)}{i\omega/\omega_0+\lambda_n}&\simeq\frac{1}{2}\int_0^1 dx\,\frac{\exp(2\pi isx)}{i\omega/\omega_0+4\sin^2(\pi x)}\\&\simeq\frac{1}{4}\sqrt{\frac{\omega_0}{\omega}}\exp\left(-\frac{i\pi}{4}-(1+i)|s|\sqrt{\frac{\omega}{2\omega_0}}\right).\end{aligned} \tag{38}$$

In deriving the first integral we have performed the $N\to\infty$ limit. The latter expression was obtained by setting $\sin(\pi x)\simeq\pi x$. Only the final result for the self-correlation function (37) is quoted here

$$\langle[\mathbf{R}_s(t)-\mathbf{R}_s(t')]^2\rangle=A(s,|t-t'|)\ 2a^2\sqrt{\frac{\omega_0|t-t'|}{\pi}}. \tag{39}$$

The time-dependent prefactor is given by

$$A(s,|t-t'|)=1-\frac{1}{2\sqrt{2\pi}}\int_0^{\infty}dx\,\frac{1-\cos x}{x^{3/2}} \tag{40}$$

$$\begin{aligned}&\times e^{-s'\sqrt{x}}[\cos(s'\sqrt{x})+\sin(s'\sqrt{x})]\\&=1-\frac{1}{4\pi}\int_0^{\infty}dy\cos\left(\frac{ys'^2}{2}-\frac{\pi}{4}\right)\frac{\ln(1+y^2)}{y^{3/2}},\end{aligned} \tag{41}$$

which scales with

$$s'\equiv\sqrt{\frac{2s^2}{\omega_0|t-t'|}}. \tag{42}$$

The complicated integral in Eq. (41) is plotted in Fig. 2. The asymptotic behavior for small values of s' is governed by the expansion

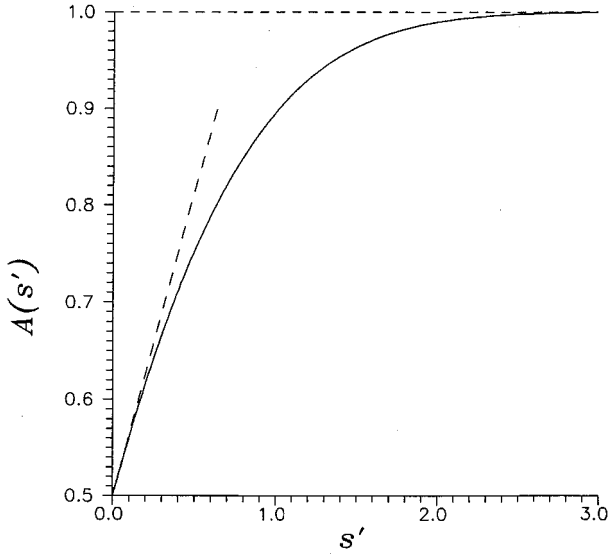

FIG. 2. Prefactor $A(s')$, Eq. (41). The dashed lines represent the asymptotic behavior for small and large values of s'.

$$A(s')=\frac{1}{2}+\frac{s'\sqrt{\pi}}{2\sqrt{2}}-\frac{s'^2}{4}+O(s'^3). \tag{43}$$

In particular for the diffusional motion of the cross-link ($s=0$), we find $A=1/2$ which is exactly half the diffusion constant of an unconstrained monomer in the Rouse model [16]. The finding is in agreement with the result in Ref. [5] based on the method of Lagrangian multipliers. For $s\to\infty$ (monomers that are sufficiently far from the cross-link) we recover the diffusion law of the classical Rouse model ($A=1$) which was first derived by de Gennes [16].

In addition, we obtain the crossover from the slower dynamics of the cross-link to that of a ''free'' monomer in the classical Rouse model as s is varied from zero to infinity. The crossover takes place on time scales of the order

$$\tau_s=s^2/\omega_0=(sa)^2/(3D), \tag{44}$$

where sa measures the distance of the monomer from the cross-link (Fig. 3). Interestingly a monomer begins to feel the presence of the cross-link only after a timespan of the order τ_s.

The two limiting cases $A=1/2$ relevant for the slower dynamics of the cross-link and $A=1$ for the ''free'' chain segments far away from the cross-link are expected on physical grounds (dashed lines in Fig. 3). An ''inner'' chain segment has only two neighbors, whereas the cross-link is surrounded by four neighbors. Thus, in general, for a monomer with functionality f a prefactor $A(f)=2/f$ is expected, as was pointed out previously [5].

VI. CONCLUSION

Within the framework of the Rouse model we have proofed that an exact solution for the Langevin dynamics of a polymer subject to *hard* δ constraints exists when excluded volume and hydrodynamic forces are neglected. The fundamental and general result for the resolvent, Eq. (25), was derived for an arbitrary cross-link configuration making our results also applicable to the challenging problem of a random network.

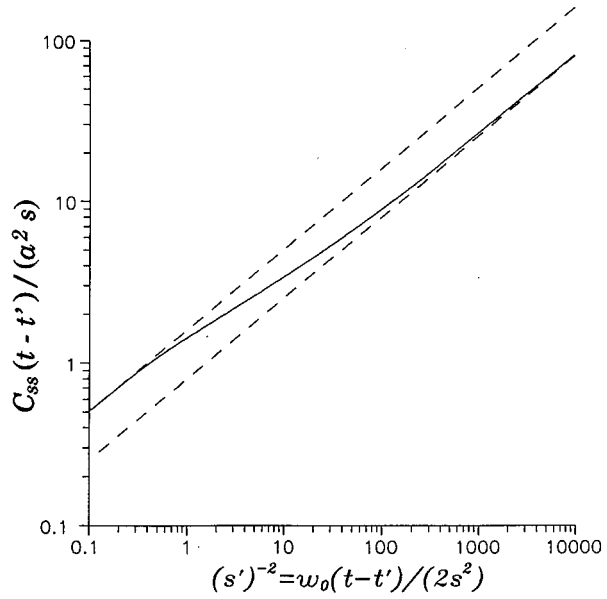

FIG. 3. Crossover of the mean squared displacement from the dynamics of a ''free'' Rouseian monomer (upper dashed line) to the slower dynamics of a cross-link (lower dashed line).

In this investigation we restricted ourselves to the simplest physical scenario, where only Rouseian dynamics was involved. This case was deliberately chosen to highlight the principal mathematical difficulties. As a special application we studied the dynamics of the figure-eight-shaped polymer depicted in Fig. 1(a). In contrast to an earlier attempt by Warner [5] based on Lagrangian multipliers which yielded only two limiting cases $s\to 0$ and ∞, the full solution could be derived by our method. Moreover, our result allows for computation of the dynamic scattering function [16] and comparison with experimental data taken in the dry network state. A detailed comparison will be studied in a future, less formal paper.

For the physically more realistic scenario of a swollen network in a theta solvent further generalizations are required, such as taking hydrodynamic interaction into account. A generalized version of the equation of motion (1) would read

$$\zeta\frac{d\mathbf{R}_i(t)}{dt}=\sum_j \mathbf{\Theta}_{ij}(-\nabla_{\mathbf{R}_j}\mathcal{H}_0(\{\mathbf{R}_j\})+\mathbf{F}_j(t)), \tag{45}$$

where $\mathbf{\Theta}_{ij}$ is the Oseen tensor. Although the above equation becomes analytically untractable, for most experimental situations a preaveraged treatment is well justified [4]. This computation is left for future work.

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